



## EVALUATION OF THREE WATERSHED-SCALE PESTICIDE ENVIRONMENTAL TRANSPORT AND FATE MODELS<sup>1</sup>

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**ABSTRACT:** The U.S. Environmental Protection Agency (USEPA) Office of Pesticide Programs (OPP) has completed an evaluation of three watershed-scale simulation models for potential use in Food Quality Protection Act pesticide *drinking* water exposure assessments. The evaluation may also guide OPP in identifying computer simulation tools that can be used in performing aquatic ecological exposure assessments. Models selected for evaluation were the Soil Water Assessment Tool (SWAT), the Nonpoint Source Model (NPSM), a modified version of the Hydrologic Simulation Program-Fortran (HSPF), and the Pesticide Root Zone Model-Riverine Water Quality (PRZM-RIVWQ) model. Simulated concentrations of the pesticides atrazine, metolachlor, and trifluralin in surface water were compared with field data monitored in the Sugar Creek watershed of Indiana's White River basin by the National Water Quality Assessment (NAWQA) program. The evaluation not only provided USEPA with experience in using watershed models for estimating pesticide concentration in flowing water but also led to the development of improved statistical techniques for assessing model accuracy. Further, it demonstrated the difficulty of representing spatially and temporally variable soil, weather, and pesticide applications with relatively infrequent, spatially fixed, point estimates. It also demonstrated the value of using monitoring and modeling as mutually supporting tools and pointed to the need to design monitoring programs that support modeling.

(KEY TERMS: computational methods; simulation; transport and fate; pesticide; NAWQA; SWAT; NPSM; HSPF; PRZM-RIVWQ.)

Parker, Ronald, J.G. Arnold, Michael Barrett, Lawrence Burns, Lee Carrubba, S.L. Neitsch, N.J. Snyder, and R. Srinivasan, 2007. Evaluation of Three Watershed-Scale Pesticide Environmental Transport and Fate Models. *Journal of the American Water Resources Association* (JAWRA) 43(6):1424-1443. DOI: 10.1111/j.1752-1688.2007.00101.x

### INTRODUCTION

The Food Quality Protection Act (FQPA) was passed by the United States (U.S.) Congress in August

1996. Among other requirements, it mandates that the U.S. Environmental Protection Agency (USEPA) Office of Pesticide Programs (OPP) develop new methods to evaluate the human health risk posed by pesticide product use. The new methods under

<sup>1</sup>Paper No. J06048 of the *Journal of the American Water Resources Association* (JAWRA). Received April 10, 2006; accepted March 12, 2007. © 2007 American Water Resources Association. **Discussions are open until April 1, 2008.**

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development consider the cumulative risk posed by multiple pesticides having the same mode of toxic action and aggregate risk due to multiple routes of exposure including food and drinking water consumption and pesticide use in the home. OPP is also required by the Federal Insecticide Fungicide Rodenticide Act (FIFRA) to assess the risk posed to nontarget aquatic and terrestrial organisms due to exposure to pesticides in the environment. The OPP Environmental Fate and Effects Division (EFED) are charged with carrying out both drinking water risk assessments for FQPA and aquatic ecological risk assessments mandated by FIFRA. These risk assessments are based on comparing the estimated environmental pesticide concentrations that are expected from normal use (exposure) to known toxic concentrations based on laboratory testing (effects). A calculated exposure/effects ratio is used as an indication of potential risk both to humans and to the environment.

In order to develop pesticide exposure concentration values for use in an ecological or a human health risk assessment, the agency relies on a combination of field monitoring and computer simulation modeling. The two approaches used together have a synergy in which each compliments the other. With approximately 7,000 surface water intake locations across the U.S. and with the concentrations of more than 400 pesticides changing day-to-day and year-to-year, the cost of monitoring by itself is prohibitive. Computer simulation on the other hand, while it permits estimation of daily concentration values at many selected sites quickly and easily, has little value if the concentration values are not grounded in a known field reality. Monitored values, if collected with sufficient frequency and with contextual data, can be used to provide data points in time and in space that can be used directly in risk assessments, and possibly more importantly, may be used to develop, validate, and calibrate simulation models. Simulation models can be used to interpolate between and extrapolate beyond measured data points both in space and in time. Each method feeds the other in a way that enhances predictive ability far beyond the capacity of either one by itself.

Currently, in order to evaluate all pesticides on an equal footing, "standard" computer modeling scenarios have been developed. For FQPA public drinking water assessments, OPP uses an agricultural watershed/drinking water reservoir scenario. This scenario is based on a 173 ha watershed at Shipman, Illinois, which until recently served as a source of drinking water for the community of Shipman. For aquatic ecological assessments under FIFRA, an agricultural field/farm pond scenario was selected as a standard aquatic environment for modeling. In using this "standard pond" scenario, it is assumed that rain

falling on a 10 ha pesticide-treated, agricultural field causes pesticide-laden runoff into a 1 ha by 2 m deep water body. Daily concentration values are simulated at both the "index reservoir" and the "standard pond" sites over a 30-year period in order to provide an estimate of the day-to-day as well as the year-to-year variability of the estimates. In the computer simulations, the "index" drinking water reservoir is treated differently from the farm pond in two ways. First, the reservoir simulation takes into account the percentage of the watershed that is cropped and treated with pesticide and second, it assumes the annual mean runoff from the watershed is routed through the reservoir, which removes some pesticide through advection. Ecological assessments using the standard pond do not consider either the cropped area or flow through the pond. Computer simulations have relied largely on the USEPA Pesticide Root Zone Model (PRZM) (Carsel *et al.*, 1998) and the USEPA Exposure Analysis Modelling System (EXAMS) (Burns, 2001, 2004).

The "index drinking water reservoir" and the "standard farm pond" are used in the lower two tiers of a tiered modeling system. The tiered approach is designed to minimize the amount of analysis required to evaluate any given chemical by requiring more complex levels of investigation only for those that have not "passed" (demonstrated safety) in the next lower tier. For upper-tier assessments, more complex models and more detailed modeling scenarios can be used as more time is allocated to perform the assessments. For upper tier assessments, OPP is looking into the possibility of moving beyond use of the static farm pond and index reservoir scenarios and has begun investigating the use of watershed or basin-scale models that simulate pesticide concentrations in flowing streams and rivers as reported herein. Before adopting a flowing water model or models to use for upper tier assessments, however, it was decided to initiate an evaluation of existing basin-scale models and seek the advice of a FIFRA Science Advisory Panel (SAP) as a part of the evaluation. The objectives of the model evaluation process were (1) to assess the capabilities and accuracy of selected models to simulate pesticide fate and transport in streams and rivers and (2) to evaluate the practicality of their use in a regulatory context.

## EVALUATION METHODS

A two-part process was used for model evaluation. The first part was a survey of developers of potential useful models to obtain an initial overview of model

features and capabilities to present to the SAP. The SAP was asked to examine the available information and recommend which of the models should undergo further evaluation. The second part of the evaluation was a simulation exercise to gain experience with use and performance of the models selected by the SAP.

### *Part I: Model Survey*

A questionnaire was designed with both closed- and open-ended questions. The closed-ended questions provided a model-to-model comparison of model features and the open-ended questions allowed the model developers to elaborate on specific model capabilities. Upon completion of this survey, model developers were contacted for clarification of specific technical issues and their impact on pesticide concentration estimates in flowing water. Information collected during the survey was presented at a SAP meeting in July 1998. The materials presented to the SAP members can be viewed at: <http://www.epa.gov/scipoly/sap/meetings/1998/july/1part5.pdf>.

The members of the SAP recommended that EFED proceed with the model evaluation. The models evaluated were the Hydrological Simulation Program-Fortran/Nonpoint Source Model (HSPF/NPSM), the PRZM/Riverine Water Quality Model (RIVWQ), and the Soil Water Assessment Tool (SWAT). *Descriptions of the three selected models can be found in the JAWRA online ancillary data files* (see Supplementary Material). Neither the existing surface water regression models such as surface water mobility index (SWMI) nor deterministic models such as the USDA/Natural Resources Conservation Service (NRCS) Annual AGricultural Nonpoint Source (AnnA-GNPS) model were sufficiently well developed to be evaluated at the time this project began. Neither had developed geographic information system (GIS) linkages to soil or weather databases at that time. The EFED contracted with the developers of PRZM/RIVWQ and SWAT and with an experienced HSPF/NPSM modeler to perform the simulations, which were carried out as part of the second phase of the evaluation.

### *Part II: Model Evaluation*

The second part of the evaluation, which was carried out following the recommendations of the SAP, was a comparative simulation exercise with the goal of establishing the relative accuracy and usability of the recommended models. In planning for this part of the evaluation, OPP consulted with the U.S. Geological Survey (USGS) regarding potential sites that would

be suitable for the comparative work in terms of providing field data for model calibration and performance testing. USGS recommended the Sugar Creek and the Kessinger Ditch watersheds in the White River Basin in Indiana. The White River Basin forms part of a study unit of the National Water Quality Assessment (NAWQA) program (Gilliom *et al.*, 1995). For cost reasons, data from the Sugar Creek watershed only were used in the model evaluation. Flow, sediment, and monitored pesticide concentration data were available for 1992 through 1996, thus the model assessment was based on these years of data.

Increasing levels of uncalibrated followed by calibrated simulations were used in the evaluation to provide experience with the levels of effort required for the models to be useful in regulatory assessments. The first level was a set of completely uncalibrated or “cold” model runs. These are model runs that are completely uninformed by any knowledge of monitored flow or pesticide concentration data from the site. The second level included calibration to measured flow from 1992 followed by a “cold” simulation of atrazine for that year. The next level of simulation involved calibration to the 1992-atrazine data followed by simulation of the pesticide atrazine concentrations for the period 1993–1995. This procedure was then repeated for the pesticides metolachlor and trifluralin. Atrazine and metolachlor were chosen as representatives of mobile pesticides. Trifluralin was chosen to represent a pesticide that is tightly bound to soil and to stream bottom sediments and is much less mobile than the other two.

This project uses the term “model evaluation” rather than “model validation” to indicate a process that is wider than that of validation. This evaluation includes not only measures of agreement between monitored and modeled concentration values (validation), but also considers ease of use of the model, cost, and applicability of the modeling results in a regulatory setting.

### *Description of Sugar Creek Watershed Site and Monitoring Data*

The study watershed is located in the White River Basin near New Palestine, Indiana, approximately 25 km east of Indianapolis (Figure 1). Sugar Creek, a perennial stream in the Basin, drains 242 km<sup>2</sup> upstream of New Palestine. Sugar Creek flows into the Driftwood River, a tributary to the East Fork White River, about 60 km downstream from New Palestine. The Sugar Creek watershed was one of several small basins chosen for study in the White River Basin to represent different combinations of homogeneous natural features and land use (LU) (Gilliom *et al.*, 1995). In particular, it was chosen



FIGURE 1. The White River Basin, Indiana.

because it is dominated by agricultural LU and has poorly drained soils, making it representative of large areas of Indiana and the Midwest.

The Sugar Creek watershed is a flat, narrow, elongate shaped basin approximately 5 km wide and 50 km long (Figure 2). Using Basinsoft (Harvey and Eash, 1996), the characteristics of the Sugar Creek watershed were determined. The elevation at the sampling site is 241 m. Maximum relief in the basin is 86 m. The length of the main channel is 69 km; channel slope is about 1.1 m/km. Drainage density is 0.41 km of stream length per square kilometer of watershed area.

As many as three different glacial episodes occurred in central Indiana. Sugar Creek lies in the Tipton Till Plain, a flat to gently undulating glacial depositional plain of Wisconsin Age. Soils in the Sugar Creek watershed are mapped primarily as part of the Crosby-Brookston soil association – poorly drained, nearly level, loamy soils developed on Wisconsin glacial tills (USDA-SCS and Purdue University Agricultural Experiment Station, 1982). Much of the cropland in the Sugar Creek watershed is artificially drained as it is the most poorly drained cropland in Indiana. Fifty percent of cropland in Indiana is drained either with ditches or tile drains (U.S. Department of Agriculture, 1987).

The 1971-2000 average annual precipitation in east-central Indiana was 102 cm. Precipitation is fairly evenly distributed throughout the year. Typically precipitation is steady and of long duration in winter and early spring and short, but of high

intensity, in late spring and summer. At the National Weather Service rain gage several kilometers east of Sugar Creek in Greenfield, Indiana, precipitation was slightly above average in 1992 (108 cm). This slightly above average year was followed by one very wet year (133 cm in 1993) and two years of slightly below-average precipitation (93 and 98 cm in 1994 and 1995, respectively). The average annual runoff of Sugar Creek at New Palestine between 1971 and 2000 was 37.4 cm. Annual runoff followed the precipitation pattern during the study – 1992 was about average (39 cm), 1993 was well above average (59 cm), and 1994 and 1995 were below average (24 and 28 cm, respectively).

Land use in the Sugar Creek watershed, upstream from New Palestine, is 95% agriculture (Crawford, 2001). Most of the agricultural land is used for row-crops. The principal crops are corn, soybeans, and to a much lesser extent, alfalfa and wheat. Both conventional and conservation tillage systems are common in the Sugar Creek watershed. Agricultural pesticide use in the Sugar Creek watershed is similar to that in other watersheds in central Indiana with similar soils and crops. Herbicides applied to corn and soybeans dominate pesticide use in central Indiana. Herbicides are applied in the spring during planting to virtually the entire corn and soybean

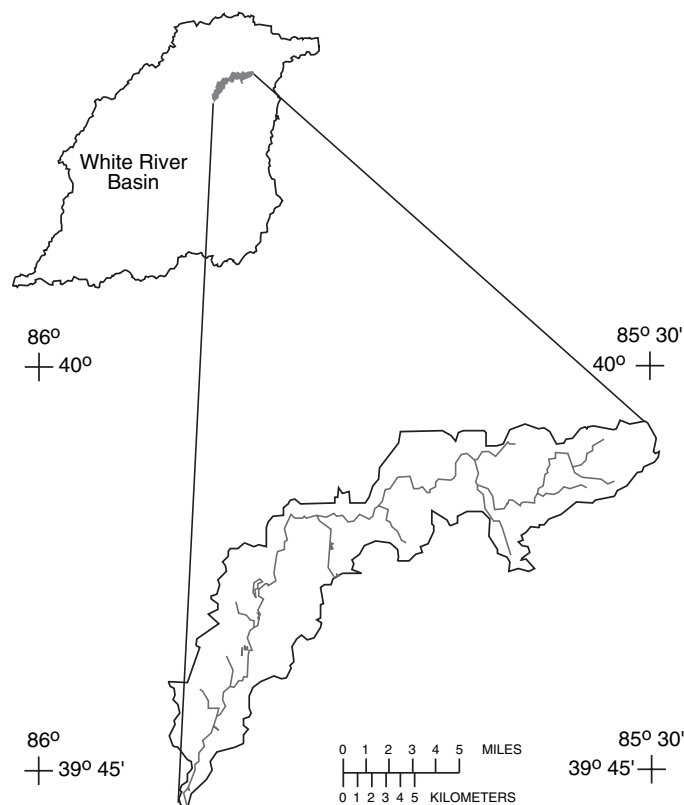


FIGURE 2. The Sugar Creek Watershed, Indiana.

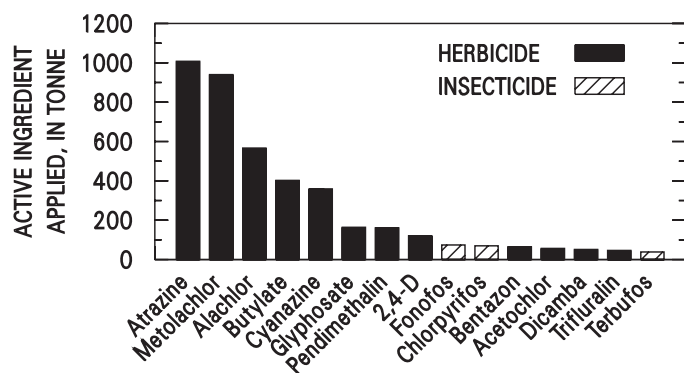


FIGURE 3. Estimated Use of the 15 Most Common Agricultural Pesticides in the White River Basin, Indiana. [1992-94 average annual usage, except acetochlor, which is 1994 usage. Source of data: Anderson and Gianessi (1995).]

crop. Insecticides are applied during the summer to about 25% of the corn crop and typically are not applied to soybeans. Triazine (primarily atrazine and cyanazine) and acetanilide (primarily acetochlor, alachlor, and metolachlor) compounds are the most used. The estimated agricultural use of pesticides in the White River Basin is shown in Figure 3. Herbicide use on corn accounts for about 70% of the total agricultural use of pesticides in the basin (Anderson and Gianessi, 1995). About 96% of the total agricultural pesticide use is herbicide and insecticide use on corn and soybeans.

#### Methods of Sample Collection and Analysis

Sample collection as part of the NAWQA program began in May 1992 at Sugar Creek. A total of 88 samples for determination of pesticide concentrations were collected through December 1995. Depth- and width-integrated samples were collected approximately weekly during May through August (except in 1994 when samples were collected approximately every two weeks) and approximately monthly during the rest of the year. Samples were collected and processed following procedures described by Shelton (1994). Samples were analyzed by gas chromatography/mass spectrometry for selected pesticides at the USGS National Water Quality Laboratory in Arvada, Colorado (Zaugg *et al.*, 1995) or by high performance liquid chromatography diode array detection (Werner *et al.*, 1996).

#### Patterns of Pesticide Occurrence in Sugar Creek

Forty-two of 78 pesticides analyzed were detected at least once in Sugar Creek from mid-1992 through 1995. Twenty or more pesticides were detected in 3%

of the samples, 13 or more in 25% of the samples, and 9 or more in 50% of the samples. Only 14 pesticides were found in concentrations that exceeded  $0.1 \mu\text{g/l}$  and only nine had concentrations that exceeded  $1 \mu\text{g/l}$ . These nine included three triazine herbicides (atrazine, cyanazine, and simazine), three acetanilide herbicides (acetochlor, alachlor, and metolachlor), bentazon, diuron, and 2,4-D. Alachlor, atrazine, metolachlor, prometon, and simazine were detected in at least 75% of the samples. Atrazine and metolachlor were found in the highest concentrations and were detected in all 88 samples collected during the study period.

Concentrations of the two most commonly used agricultural pesticides (atrazine and metolachlor) and one lesser used but frequently detected pesticide (trifluralin, found in 43% of samples) in the Sugar Creek Watershed within the White River Basin in the early 1990s are shown in Figure 4. Peak pesticide concentrations in the creek follow a yearly pattern that is related to the timing of pesticide application in the spring and the first rainfall and subsequent runoff following application. Concentrations decrease through the summer and by fall are generally low or below detection limits of the analytical method used to determine concentrations until the following spring. Pesticide occurrence in Sugar Creek generally is related to pesticide use in central Indiana. The two most used pesticides are the two most commonly found pesticides in the creek; the five most commonly used pesticides are among the twelve most frequently detected pesticides in the creek. Additional information about the occurrence of pesticides in the White River Basin can be found in Crawford (1995, 1997, 2001); additional information about the occurrence of pesticides in the Sugar Creek watershed can be found in Fenelon and Moore (1998). USGS streamflow data for Sugar Creek is available from the USGS NWIS-Web system for Indiana (<http://www.waterdata.usgs.gov/in/nwis/>).

#### Chemical Application Data

Daily usage estimates of atrazine, metolachlor, and trifluralin in the Sugar Creek watershed were based upon inferences from weekly percent crop planted and from information on timing of application in relationship to timing of planting using pre-plant and at-plant estimates.

Common modeling assumptions were developed for consistency between the three models. Sugar Creek is a USGS indicator site for the till plane area and is mostly in Hancock County. The watershed was assumed to be 95% agriculture with an equal mixture of corn and soybeans. It was further assumed that 95%

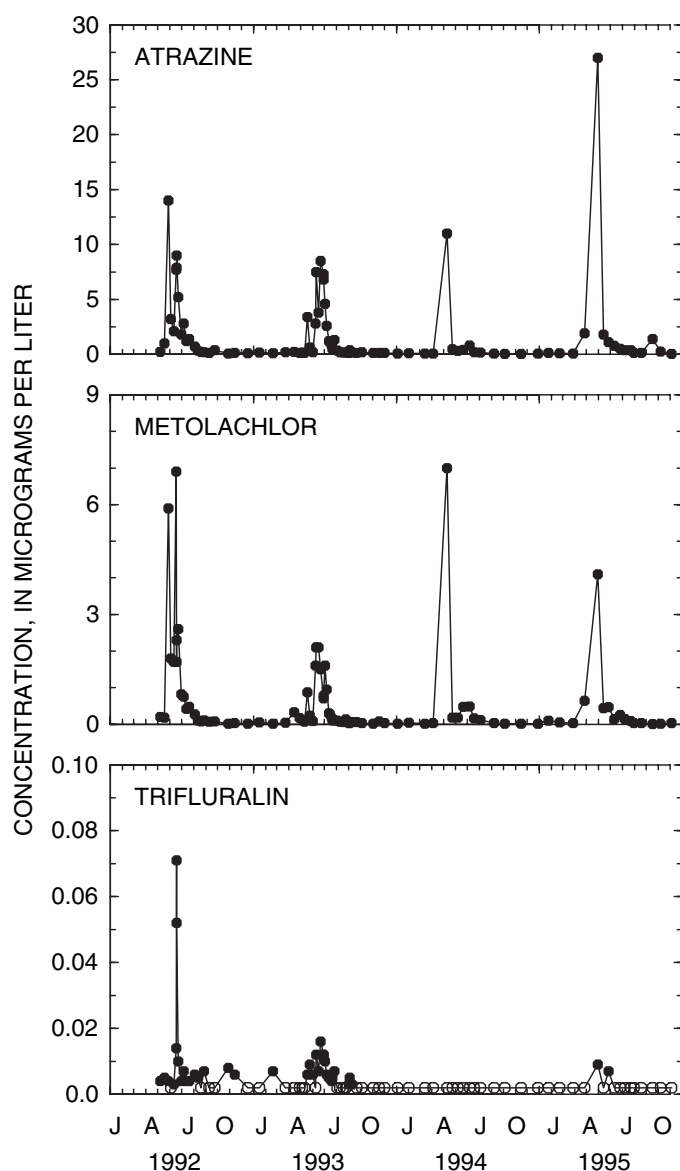


FIGURE 4. Relation of Selected Herbicide Concentrations to Time in Sugar Creek Near New Palestine, Indiana. [An open circle indicates the concentration is less than the detection limit, and therefore less than the concentration shown.]

of the atrazine agricultural usage is on corn and that 87% of the corn in the watershed is treated with atrazine at average rate of 1.35 pounds of active ingredient per acre. Both corn and soybeans in the watershed are 100% straight plow and 100% artificially drained with a six to twelve inch tile drainage system. Ten percent of the watershed is in conservation tillage.

Soil Water Assessment Tool modelers provided consistent trapezoidal channel geometries from the USEPA Reach File 1 database (top width, bottom width, slide slopes, and depth to top width) and provide locations where cross-sections were taken. Soils data from the USDA STATSGO database were judged to have adequate resolution and were used in the

simulation. In calculating channel friction, it was assumed that the channels are silt, sand, and gravel with very little weeds or stones and that impoundments and other attenuating features are negligible. USGS streamflow data for Sugar Creek is available from the USGS NWISWeb system for Indiana (<http://www.waterdata.usgs.gov/in/nwis/>).

#### *Pesticide Environmental Fate Input Data*

Environmental fate data needed as input to the models were provided by USEPA based on data submitted by the pesticide manufacturers for each chemical. Environmental fate modeling inputs used by each of the three models is described in Table 1. In some cases, other values were used if they were deemed by the modeler to be more appropriate.

#### *Estimations of Daily Pesticide Usage and Model Inputs*

A number of assumptions were made in order to calculate daily application amounts for each of the three pesticides on farms in the Sugar Creek basin. All three pesticides used in model simulations were predominantly corn and soybean herbicides: total usage was near 100% on corn alone for atrazine, near 100% on corn and soybeans combined for metolachlor, and 95-98% on soybeans for trifluralin (with the remaining 3-5% representing minor crop agricultural and nonagricultural use; the exception to this was 1996, when trifluralin was generally not applied to soybeans in Indiana). The following data sources were utilized:

(1) Planting date information (Indiana Agricultural Statistics Service 1993, 1994, 1995, 1996) was used as a reference point for estimating pesticide application dates for soybeans and corn. These periodic amounts (at 7- to 10-day intervals) were transformed to daily values assuming a uniform distribution.

(2) Application dates were referenced to the planting dates using assumptions based on expert local opinion (Thomas T. Bauman, Department of Botany and Plant Pathology, Purdue University, West Lafayette, Indiana, 1998, personal communication; Dowdy, 1998; Petersen, 2000) and the final product was reviewed for reasonableness by the Hancock County Extension Agent where the Sugar Creek watershed is located.

(3) For the corn and soybean use areas, pesticide application loads each year were calculated utilizing annual statewide estimates of percent crop treated and average application rate (USDA-NASS, 1993, 1994, 1995, 1996, 1997) censuses of corn and soybean acreage in Hancock County (U.S. Department of

TABLE 1. Pesticide Environmental Fate Modeling Input Parameters.

Input Parameter (Units)	Pesticide		
	Atrazine	Metolachlor	Trifluralin
Aerobic Soil Metabolism Half-Life (days)	140	6.9 to 21 days, 30.6 after	169
Anaerobic Soil Metabolism Half-Life (days)	578	80.9	42
Soil Photodegradation Half-Life (days)	12	78.8	
Aerobic Aquatic Metabolism Half-Life (days)		39.0 until 21 days, 24.0 after	30
Anaerobic Aquatic Metabolism Half-Life (days)	578	78.2	3
Aquatic Photodegradation Half-Life (days)	1.04	70.0	0.35
Hydrolysis Half-Life (days)	Stable	Stable	Stable
Adsorption ( $K_d$ )	0.73	2.2	
Adsorption ( $K_{oc}$ )	155.3		7,200
Vapor Pressure (torr)	3.0e-7	2.8e-5	1.84e-4
Solubility (mg/l)	33	480	0.3
Molecular Weight	215.7	283.5	335.5

Commerce, 1994 and USDA 1999), and annual state-wide estimates of corn and soybean acreage (Indiana Agricultural Statistics Service 1993, 1994, 1995, 1996, 1997). Whenever necessary, strict proportionality was assumed in transferring crop acreage data from year to year or from state or county level to the Sugar Creek basin. For minor crop use, the chief source document was a usage survey commissioned for the White River basin by the USGS NAWQA program (Anderson and Gianessi, 1995).

(4) The survey relied on publicly available documents from USDA as well as interviews with Indiana experts on agricultural uses of pesticides. Their estimates were based upon sources covering the period 1990-1993. This project's updated interviews with local experts did not identify any significant increases in production in Indiana of any of the minor use sites for atrazine, metolachlor, and trifluralin. In addition, the project consulted internal USEPA documents for estimates of nonagricultural usage of these pesticides. Unfortunately, there were no local or even-statewide estimates of nonagricultural uses available. From assuming nonagricultural usage to be proportional to the population in a given area, it was determined that nonagricultural usage was likely to be only a small percentage of the overall usage of these pesticides in Sugar Creek basin. Minor uses of trifluralin were accounted for by assuming a total of 60 lbs of trifluralin application was superimposed over the distribution calculated for trifluralin for soybean applications. This assumption was made for each year that was simulated as there was no basis for enumerated year-to-year changes in minor uses from the available data.

An example of the input tables prepared for calculations of annual basin loadings is provided for metolachlor in Table 2. The basin-level inputs thus calculated were combined with the data from Sources 1 and 2 noted above to prepare daily basin loadings for the three pesticides simulated as shown in Figure 5 (atrazine), Figure 6 (metolachlor), and Figure 7 (trifluralin).

The daily pesticide basin application values were calculated using linear interpolation between reported values for percent crop planted and uniform distribution of herbicide application dates over a fixed window (for atrazine on corn this was the 14 days following planting) in reference to the crop planting date. For example, for atrazine in 1992, it was estimated that 1.7, 4.2, and 62.3% of the corn crop was planted by April 20, April 30, and May 10, respectively (Indiana Agricultural Statistics Service, 1993). Corn is the only significant crop on which atrazine is used in Sugar Creek basin. Atrazine applications were distributed evenly over the first 14 days after application so the daily atrazine loadings were dependent upon the daily acreage of soybeans planted over the previous 14 days. The effect of these calculations is illustrated in Table 3, which shows the daily atrazine loadings (i.e., pounds applied to the Sugar Creek watershed) calculated over this period in 1992 along with the interim calculations for cumulative percent soybean crop planted, daily percent crop planted, and daily percent (of total annual) atrazine applied. This procedure is likely to provide reasonably accurate estimates of the loadings plus or minus a few days. The chief limitation is that it does not account for specific events on a particular day (such as steady rain all day) that might shift a significant amount of the herbicide applications by a few days.

#### *Land Use/Land Cover Data*

Multi-Resolution Land Characterization Thematic Mapper data was not available for Indiana. USGS Land Use/Land Cover (LU/LC) was available through the SWAT model and was used in the simulations by all three models. These data are also available in better assessment science integrating point and non-point sources (BASINS) for use in

TABLE 2. Annual Basin Application Rate Calculations – Metolachlor.

	1992	1993	1994	1995	1996
<i>Corn Data</i>					
Hancock County Area (acres)	2,01,557	2,01,557	2,01,557	2,01,557	2,01,557
Hancock Corn Acreage	71,600	63,300	70,000	64,400	63,700
Sugar Creek Basin Area	60,096	60,096	60,096	60,096	60,096
% Corn Treated, Statewide	31	35	43	31	30
Treated Acres in Basin	6,618	6,606	8,975	5,952	5,698
Average Application rate (lb ai/A)	1.92	1.90	1.88	1.85	1.92
Basin Corn Application Amount (pounds)	12,706	12,551	16,872	11,012	10,940
<i>Soybean Data</i>					
Hancock County Area	2,01,557	2,01,557	2,01,557	2,01,557	2,01,557
Hancock Soybean Acreage	66,300	72,200	67,100	70,100	81,900
Sugar Creek Basin Area	60,096	60,096	60,096	60,096	60,096
% Soybean Treated, Statewide	13	14	8	9	2
Treated Acres in Basin	2,570	3,014	1,601	1,881	488
Average Application Rate (lb ai/A)	2.02	1.86	1.99	2.13	1.78
Basin soybean Application Amount (pounds)	5,191	5,606	3,185	4,007	869
<i>Overall Basin Usage Calculations</i>					
Total Treated Acres in Basin	9,188	9,619	10,575	7,834	6,186
Total Basin Application Amount (lbs)	17,897	18,156	20,057	15,019	11,809
% of Basin Usage on Corn and soybean	100	100	100	100	100
% of Basin Treated With Metolachlor:	15.3	16.0	17.6	13.0	10.3
Basin-Wide Application Rate (lb ai/A)	0.298	0.302	0.334	0.250	0.197

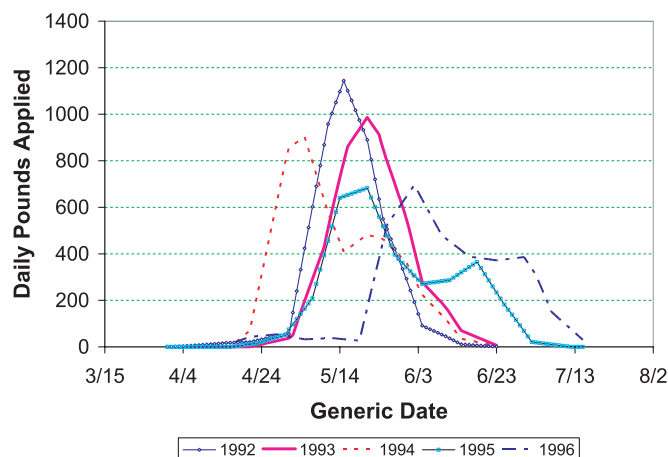


FIGURE 5. Estimated Daily Atrazine Applications in the Sugar Creek Basin, 1992-1996 (data: Indiana Agricultural Statistical Service).

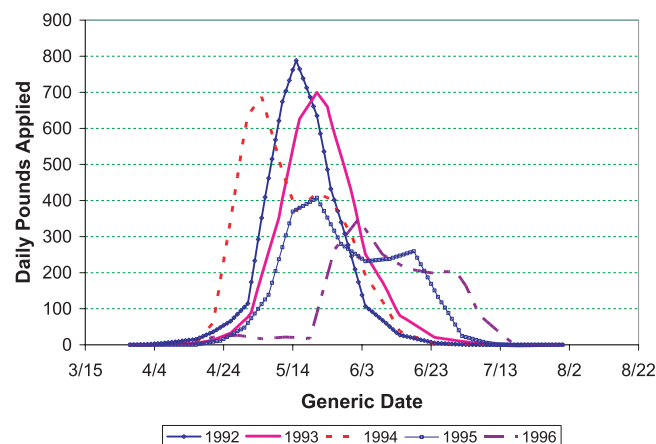


FIGURE 6. Estimated Daily Metolachlor Applications in the Sugar Creek Basin, 1992-1996 (data: Indiana Agricultural Statistical Service).

NPSM. This identifies land as agricultural only and is not crop specific. The SWAT modelers discretized the watershed using the Digital Elevation Model (DEM) in SWAT and distributed it in ArcView format to other modelers in order to have a consistent representation of the watershed.

#### Weather Data

There are five weather stations located in the area that contributes runoff to the Sugar Creek watershed. They are listed in Table 4 with the county in

which they occur. The areas assumed to receive rainfall from each weather station were delineated by drawing a polygon around each station with boundaries equal distances from the nearest stations. The portion of the watershed within each polygon was assumed to contribute runoff to the stream based on the rainfall for that weather station.

#### Description of Modeling Procedures

**NPSM Model Input Development and Calibration Procedure.** The first step in NPSM calibration

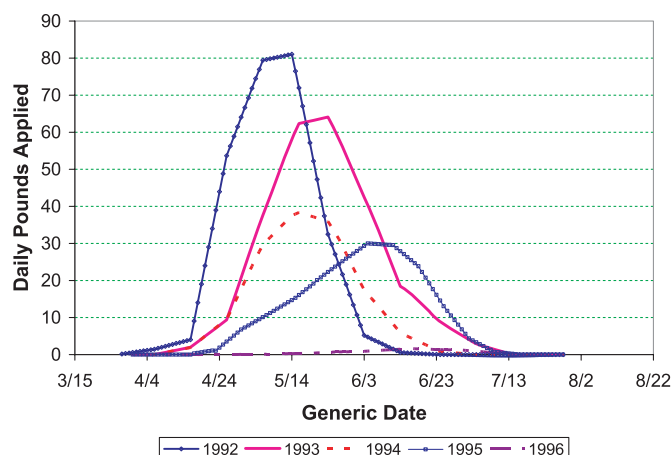


FIGURE 7. Estimated Daily Trifluralin Applications in the Sugar Creek Basin, 1992-1996 (data: Indiana Agricultural Statistical Service).

is hydrologic calibration. However, prior to parameterization of the model with values specific to the Sugar Creek watershed uncalibrated runs were performed in order to assess whether there were obvious errors in storm-flow or base-flow simulation to determine which parameters were most in need of adjustment. Simulation runs for hydrologic calibration were performed for the period January 1, 1990, through December 31, 1992. Although USEPA selected 1992 as the time period to be used for model calibration, multiple years were selected in order to lessen the influence of extreme years and enable a more

TABLE 4. Weather Stations.

Weather Station Name	County Location	Station Reference Number
Indianapolis	Marion County	124272
Greenfield	Hancock County	123527
Freelandville	Knox County	123104
Vincennes 1	Knox County	129112
Vincennes 2	Knox County	129113

accurate representation of average flow patterns. Model predicted flows were compared graphically and statistically to USGS historical streamflow daily values. The statistical tests chosen were the Mann-Whitney Rank Sum Test, which compares median values, and the Wilcoxon Signed Rank Test, which performs a pairwise comparison, both of which are nonparametric tests because flow data are not normally distributed, and the Nash-Sutcliffe (NS) coefficient on log-transformed values. The first calibration step consisted of changing the values of parameters to estimated values using the guidelines written by the developers of BASINS. Parameter estimates were made using spatial data on LU, topography, and soils contained in BASINS as well as from soil and crop data in the National Resources Inventory database. The output from this run was also compared with USGS data statistically. Based upon the results, parameters that most affect the water balance, such as lower zone soil moisture, infiltration (INFILT), and interflow (INTFW) were adjusted until there was

TABLE 3. Example of Daily Herbicide Watershed Loading Calculations: Atrazine Applied to Sugar Creek Watershed Between April 20 and May 10, 1992.

Date	Cumulative % Planted	Daily % Planted	Daily % Application of Chemical	Daily Atrazine Applied (lbs)
20 April 92	1.7	0.1	0.09	20.06
21 April 92	2.0	0.3	0.09	20.60
22 April 92	2.3	0.3	0.11	24.39
23 April 92	2.6	0.3	0.12	28.19
24 April 92	2.9	0.3	0.14	31.98
25 April 92	3.2	0.3	0.16	35.78
26 April 92	3.5	0.3	0.17	39.03
27 April 92	3.8	0.3	0.19	42.28
28 April 92	4.1	0.3	0.20	45.54
29 April 92	4.4	0.3	0.21	48.79
30 April 92	4.67	0.3	0.23	52.04
1 May 92	10.4	5.8	0.24	55.29
2 May 92	16.2	5.8	0.65	147.45
3 May 92	22.0	5.8	1.05	239.60
4 May 92	27.7	5.8	1.46	331.76
5 May 92	33.5	5.8	1.86	423.91
6 May 92	39.3	5.8	2.25	512.82
7 May 92	45.0	5.8	2.64	601.72
8 May 92	50.8	5.8	3.03	690.62
9 May 92	56.6	5.8	3.42	779.53
10 May 92	62.3	5.8	3.81	868.43

no statistically significant difference between NPSM predicted flow and USGS gauge data for the outflow point of the selected watershed (see Carrubba, 2000 for additional details.) Once flow data were calibrated, the sediment module in NPSM was activated. However, due to a lack of NAWQA sediment data for the calibration period, no calibration of this module was performed. After the sediment module was activated, calibration of the pesticide module was begun. Atrazine was chosen as the pesticide to be modeled first in the Sugar Creek basin and an uncalibrated run of the model was completed for this pesticide because the NPSM default data file contains parameter values for this pesticide. NPSM was run separately for each pesticide. For each pesticide simulation, the single value Freundlich isotherm method was chosen for simulation of the adsorption/desorption process. The first parameters adjusted as part of the calibration process were those related to the Freundlich equation. Three phases of pesticides in the soil are possible in this method: crystalline, adsorbed, and solution. These phases are further separated on the basis of soil layers such that separate values are required for the surface, upper, lower, and ground-water layers. The default values for these parameters are zero in NPSM except for atrazine, which is part of the model's default dataset. Following adjustment of the Freundlich isotherm equation values, degradation rate parameters were adjusted for the surface, upper, lower, and ground-water layers on the basis of pesticide chemical properties. Because trifluralin is highly volatile, the volatilization subroutine was activated for this pesticide and the parameter value set based on the volatilization rate reported in the *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals*, Vol. 5 (MacKay *et al.*, 1997).

**RIVWQ Model Input Development and Calibration Procedure.** The PRZM component of the model was first configured in a relatively simplistic representation of the watershed to make atrazine-only simulations with the predominately agricultural watershed represented as either corn or "other." When the two additional chemicals were incorporated (metolachlor and trifluralin), modifications to the cold run were made to include the necessary soybean (the additional crop receiving chemical applications) LU and the modified cold run scenarios were run for all chemicals. The model was calibrated to 1992 data before being used for the final validation period of 1993-1995. PRZM simulations were utilized to represent the variable soils, crops, and weather conditions throughout the watershed and were combined for each subwatershed based on the LU and soil distribution within the subwatershed. The predicted mass of

each chemical and volume of water runoff were input to the nodes of the RIVWQ Sugar Creek simulation.

The watershed was subdivided into smaller analysis units (subwatersheds) of similar crop and soil characteristics for PRZM simulations, which serve as inputs to the RIVWQ link node network. Watersheds were subdivided to provide smaller and more uniform computational units. The channel system was segmented into a series of nodes and links, which are the computational elements used in the solution scheme of RIVWQ. Nodes were represented along the channel system with link lengths ranging from 500 to 3,974 m. Node spacing was based on resolution and numerical stability considerations. Channel geometry and slope were obtained from the SWAT groups modeling effort. Drainage basins contain natural and anthropogenic storage areas that hold water and retard the flushing of waterborne constituents. These areas result from factors such as farm ponds, channel depressions, side pools, beaver dams, fallen trees, and other obstacles or impediments and are not specifically or individually represented, rather the input parameter depression storage (DS) in RIVWQ was used in the simulations to account for the cumulative impact of these factors. An initial value of  $150 \text{ m}^3$  was set for DS for each channel segment. With DS, stored residues are continuously mixed with, and eventually replaced by, upstream flows. Residue attenuation is inversely proportional to flow rate and directly proportional to storage volume. Streamflow includes base flow (set to  $0.000695 \text{ m}^3/\text{s}/\text{km}^2$  of drainage area) and runoff sources. Base flow and dead storage were set based on professional judgment with calibration adjustment anticipated. Storm runoff was predicted by PRZM for both treated and untreated areas. Water runoff from untreated areas was assumed to respond similarly to treated areas (i.e., based on the same curve number). Weather data, precipitation, and temperature was from the National Oceanographic and Atmospheric Administration (NOAA) station at Greenfield, Indiana (123527) located south of the central part of the watershed. Additional stations were added to subsequent simulations summarized below.

The provided application rate on corn was multiplied by the percent corn treated (statewide) so 100% treatment at the reduced rate as a model input is equivalent to the 1992 atrazine application on 79% treated at the average rate (1.35 lb active ingredient per acre). The total chemical mass in the watershed was maintained. Drift was computed as 1% of the applied, assuming 50% of the fields along the stream could potentially receive applications at the same fraction as the watershed. Drift was a function of the segment width and length. Environmental fate properties were represented as provided by USEPA to all

modeling groups and summarized previously. Atrazine PRZM environmental fate parameters include an average  $K_{oc}$  of 87.8, soil photolysis of 12 days used in the top 2 cm of soil, aerobic soil metabolism of 146 days, and anaerobic soil metabolism of 159 days; atrazine RIVWQ environmental fate parameters include aquatic metabolism of 578 days in water and 330 days in sediment and a solubility of 33 ppm.

The two predominant soils for each county (Hancock and Henry) were simulated. One soil was common to each county, resulting in the selection of three representative soils being used for the watershed. The county distribution was utilized for the subwatersheds falling primarily in these two counties. Soils properties from the NRI92 (USDA, 1994a) and SOILS5 (USDA, 1994b) databases, confirmed by the soil surveys for the two primary counties provided a representation of the Sugar creek watershed. Soil properties for the Brookstone, Crosby, and Cyclone series were obtained from the SOILS5 database (USDA, 1994b). Values for field capacity and wilting point were obtained using the methods contained in DBAPE, the Database Analyzer and Parameter Estimator Interactive Computer Program (Imhoff *et al.*, 1990).

After preliminary calibration attempts, and the need to accommodate metolachlor and trifluralin application data, modifications to the original LU representation were needed. The initial soybean/other land-use was divided to a soybean only LU to enable the representation of metolachlor (both corn and soybean applications) and trifluralin (soybean only applications). An addition "other" LU was added for the representation of nonagricultural areas (grasses/woods/barren, etc.). Each subwatershed was assigned to one of four meteorological stations rather than the initial single station representation. The stream network did not change although initial calibration runs indicated the need for an increase in base flow to  $0.001745 \text{ m}^3/\text{s}/\text{km}^2$  of drainage area and DS was allowed to vary between 40 and  $520 \text{ m}^3$  as a function of drainage area. Predicted lateral flow from PRZM was also incorporated as a source of water and chemical loading to the river network (representative of the extensive drain tile network in the watershed).

Environmental fate parameters remained the same for atrazine. Metolachlor PRZM environmental fate parameters include an average  $K_{oc}$  of 200, soil photolysis of 78.8 days used in the top 2 cm of soil, aerobic soil metabolism of 30.6 days, and anaerobic soil metabolism of 80.9 days; metolachlor RIVWQ environmental fate parameters include aquatic metabolism of 39 days in water and 78.2 days in sediment and a solubility of 48 ppm. Trifluralin PRZM environmental fate parameters include an average  $K_{oc}$  of 7,200, aerobic soil metabolism of 169 days, and anaerobic soil metabolism of

42 days; trifluralin RIVWQ environmental fate parameters include aquatic metabolism of 30 days in water and three days in sediment and a solubility of 3 ppm. Application data (rates and dates) for metolachlor and trifluralin were compiled similarly to the atrazine data and summarized previously.

A final calibrated model was developed through limited iterative parameter modification by visual comparison between predicted and observed results following each parameter modification. The hydrology calibration parameters include changes to the Muskingum routine K values, modification to the lateral flow parameters (representing tile drains) for the corn simulations and removal of lateral flow loadings from soybean LU areas, additional dead storage to increase attenuation, and a reduction in the number of meteorological stations utilized to three (Greenfield, Anderson, and Knightstown). The application dates were shifted for all calibrated simulations to occur earlier and at a slightly compressed timing based on the central Indiana reporting district data, rather than the combination eastern and central reporting district data utilized for the previous simulations and as outlined in the application summary section. Atrazine environmental fate parameters were adjusted to reflect values seen in many additional literature studies (Giddings *et al.*, 2005). No modifications were made to the environmental fate parameters for the metolachlor and trifluralin simulations. These adjustments were all within the range of available data and improved the predictions, while not deviating from realistic input values based on the available data.

The model calibrated to 1992 data was utilized to simulate years 1993-1995 validation period for all three chemicals with no further modifications.

**SWAT Model Input Development and Calibration Procedure.** SWAT is a physically based model and requires information about weather, soil properties, topography, natural vegetation, and cropping practices. Input data for SWAT was assembled with the SWAT2000 ArcView Interface (Diluzio *et al.*, 2002b; Neitsch *et al.*, 2002b). Model input data for topography were extracted from a DEM for the contiguous U.S. The DEM was assembled from quadrangles containing 1:250,000 scale USGS  $1^\circ$  by  $1^\circ$ , 3 arc-second data. The horizontal cell size of this data is 100 by 100 m and the vertical resolution is 1 m. Because the Sugar Creek watershed has little relief, the interface was unable to correctly predict the streamflow paths using the DEM alone. To obtain proper stream path delineation, a stream map from USGS was overlaid on the DEM and used to burn in the location of the streams in the watershed. Based on the DEM and stream path map themes, the SWAT2000 ArcView interface divided the watershed into 23 subbasins.

Daily measured precipitation data for the simulation were obtained from five weather stations located around the watershed. The measured precipitation data were assigned to subbasins based on proximity of the station to the centroid of the subbasin. Daily temperature data from the Greenfield weather station were used for all subbasins in the watershed. Daily solar radiation, relative humidity, and wind speed values were generated from long-term monthly average data that were acquired from Indianapolis and Hartford City, Indiana.

Within each subbasin, SWAT allows hydrologic response units (HRUs) to be defined. The primary data source for the LC map was leaves-off (spring) Landsat thematic mapper (TM) data acquired between 1988 and 1994. Leaves-on (primarily summer) TM datasets were also acquired and referenced. Information for soils was obtained from the USDA-NRCS State Soil Geographic Data Base (STATSGO) (USDA – Soil Conservation Service, 1992) soil association dataset.

The Sugar Creek watershed dataset was set up to run on a daily time step given daily precipitation as input. Surface runoff was calculated using the USDA Soil Conservation Service (SCS) curve number method. The Penman-Monteith method was used to determine potential evapotranspiration. Channel water routing was performed using the Muskingum routing method.

The management scenarios for HRUs with row crops were modified to simulate a corn/soybean rotation. The row crop areas were split equally into two HRUs; one starting the simulation with a corn/soybean rotation, and the other with soybean/corn. This configuration retains the dynamics of the rotation in each HRU, while ensuring that in any given year half the row crop area will be in corn and the other half in soybeans. This is critical as atrazine is applied only to corn. A conventional tillage schedule was adopted for use in the simulation including disking and field cultivating. Accounting for the impact of tillage is important because tillage operations mix surface applied pesticides into the soil where they are unavailable for transport by surface runoff. However, pesticides within the soil profile are still available for transport by tile flow.

Tile drains were simulated in all HRUs with a corn/soybean rotation. Three input variables control the functioning of tile drains in the HRUs. The depth to the tile drain was set to 800 mm. The time to drain the soil profile was set to 24 h. The time for water to enter the channel network after entering the tiles was set to 48 h.

Management files were developed to automatically apply fertilizer (anhydrous ammonia) to HRUs with corn. The fertilizer application took place any time corn experienced a 20% reduction from optimal

growth due to nitrogen stress. The automated fertilizer algorithm attempts to apply enough nitrogen to meet crop demands. Filter strips were simulated between the application fields and streams assuming a 5 m buffer (edge-of-field or riparian).

USGS provided daily amounts of applied pesticides for the entire watershed. The daily pesticide amounts were summed to five-day totals and applied uniformly over the area simulated in the targeted crop. Multiple applications of the pesticides were simulated in the HRUs to capture the temporal distribution of pesticide application in the watershed. Atrazine was applied only to corn, while metolachlor was applied to both corn and soybeans.

Pesticide properties that govern pesticide transport and degradation are stored in two input files in SWAT: the pesticide database and the instream water quality file (.swq). Values from the Groundwater Loading Effects of Agricultural Management Systems model (GLEAMS) pesticide database were used to populate input fields in the SWAT pesticide database file. For the instream reaction rate, the aerobic soil half-life from the USDA Agriculture Research Service (ARS) pesticide database was used. Table 1 summarizes input values for all three pesticides.

Soil Water Assessment Tool incorporates algorithms that simulate the physical processes governing the movement of water, nutrients, and pesticides within a watershed. One of the principles guiding model development is the use of inputs that are physically based. As noted by Santhi *et al.* (2001), SWAT is not a parametric model with a formal optimization procedure. Inputs to the model are physically based (i.e., based on readily observed or measured information). However, there is often uncertainty in model inputs due to spatial variability, measurement error, etc. For example, soils property information obtained from NRCS Soil Survey is provided as ranges (i.e., saturated hydraulic conductivity might range from 15 to 50 mm/h). As the exact values are unknown, the model was manually calibrated within the uncertainty ranges to obtain the best model fit.

Calibration of streamflow in the Sugar Creek watershed was performed in two steps. First, the long-term water balance was calibrated to match total basin water yield by minimizing the difference in average annual flows. Second, daily measured and simulated flow data was calibrated for 1992 by minimizing the NS coefficient. The focus of the second step was to match the measured and simulated hydrograph shapes. Four parameters were modified or adjusted during the long-term water yield calibration: SCS curve number for moisture condition II (cn2), maximum canopy and depressional water storage (canmx), available water capacity (sol\_awc), and saturated hydraulic conductivity (sol\_k).

Once the long-term calibration was completed, efforts focused on matching the 1992 simulated daily flow hydrograph to the measured daily flow values recorded for the USGS streamflow gage. Total water yield (expressed as m<sup>3</sup>/year) was calibrated until simulated total water yield for 1992 was within 1% of the measured value.

Six parameters were modified or adjusted during the daily flow calibration: calibration coefficients for Muskingum channel routing (msk\_x, msk\_co1, and msk\_co2), Manning's *n*-value for the main channels (ch\_n), maximum canopy water storage (canmx), and the soil evaporation compensation factor (esco).

A total of 88 samples for determination of pesticide concentration were collected from May 1992 through December 1995 (Crawford, 2001). Although there is uncertainty in the pesticide inputs, we did not attempt to use any of these parameters for calibration. In other words, after the annual water balance and daily streamflows were calibrated, no further calibration was performed on the pesticides.

### Description of Statistical Techniques Used

Statistical tests of the results of simulation runs were designed to characterize the exposure metrics produced by each model, and to directly compare the models with the observed data from the 1993-1995 "validation" period. For each variable (flow, suspended sediment, atrazine, metolachlor, and trifluralin concentrations), we calculated the mean, standard deviation, and median of the observed and predicted values. These provide an initial sense of the general ability of the models to reproduce the 1993-1995 observed data following calibration to the 1992 observations.

For basic comparisons of the each of the model results to the observations, we calculated the mean absolute error (MAE), root mean square error (RMSE), Pearson correlation coefficient *r*, and the NS coefficient of modeling efficiency. We did not conduct a regression analysis of observed *vs.* simulated values, as this would amount to a re-calibration of the model providing little useful information beyond that already available from *r* (Legates and McCabe, 1999). The correlation coefficient was retained as one (albeit crude) measure of the models' ability to imitate the observed data.

Mean absolute error was calculated as:

$$\text{MAE} = \left( \sum |y_i - \hat{y}_i| \right) / n, \quad (1)$$

and RMSE was calculated as:

$$\text{RMSE} = \left\{ \left[ \sum (y_i - \hat{y}_i)^2 \right] / n \right\}^{0.5}, \quad (2)$$

where  $y_i$  is the *i*th observation and  $\hat{y}_i$  the *i*th simulated value. MAE and RMSE provide summary quantitative measures of relative deviation of the models from observations (Mayer and Butler, 1993).

The NS "modeling efficiency" (Nash and Sutcliffe, 1970) "NS" provides a better metric of model performance, with the advantage of an accepted interpretation of its value. NS has a maximum of 1.0 in the case of a perfect correspondence between model and observation and may take on large negative values when the correspondence is poor. Any NS < 0 indicates that the simple mean of the observations is a better predictor of observed data than is the output from the simulation model (Wilcox *et al.*, 1990). NS is calculated as:

$$\text{NS} = 1 - \sum (y_i - \hat{y}_i)^2 / \sum (y_i - \bar{y})^2, \quad (3)$$

Pesticide exposure models are sensitive to the estimated rates of application of the pesticide within the use setting, so model error is better expressed as a proportion of the observed value – a "prediction ratio" *E* also providing a metric that can be used to develop a "safety factor" for correcting model forecasts produced for chemical safety evaluations of other pesticides or in other agronomic settings. This idea can be employed to develop objective performance criteria or equivalence tests for models, as a descriptive tool, or as a means of scaling model predictions to meet some statistical criterion. It has been suggested that exposure model predictions [estimated environmental concentrations (EEC)] within a factor of two of reality should suffice for most regulatory applications (Baughman and Burns, 1980), and methods have been proposed to test models for adherence to this criterion (Burns, 1986, 2001; Parrish and Smith, 1990), or, similarly, to evaluate models for "equivalence" to observational data (Robinson and Froese, 2004). In addition, the mean and variance of the prediction ratio have been used as descriptive statistics for model validation studies (Bird *et al.*, 2002), along with a characterization of the relative ability of a 2× safety factor to achieve model predictions ≥ observed data. Here, we report the fraction of model estimates  $\hat{y}_i$  within the range ±2× (i.e., 0.5 $y_i$  to 2.0  $y_i$ ) as an additional evaluative metric of model performance.

A logarithmic transformation of the model predicted/observed data ratio is centered on zero, symmetrical in under- or overprediction and is

approximately normal. The transformed variable  $e$  is defined as

$$\begin{aligned} e &= \log_{10}(E) = \log_{10}(\text{Model } \hat{y}_i / \text{Observed } y_i) \\ &= \log_{10}(\hat{y}_i) - \log_{10}(y_i), \end{aligned} \quad (4)$$

If the model and data are in complete agreement,  $e = 0$  and  $E = 1.0$ . Values of  $e < 0$  are indicative of underprediction; values  $> 0$ , of overprediction. Both the average model error  $\bar{e}$  and its standard deviation  $Se$  measure model performance.  $\bar{E} \equiv 10^{\bar{e}}$  and  $\rho \equiv 10^{Se}$  are also of interest:  $\bar{E}$  is the geometric mean under- or overprediction ratio, and  $\rho$  is a multiplicative factor such that as  $e$  takes the range  $\bar{e} \pm Se$ ,  $E$  varies from  $\rho^{-1}\bar{E}$  to  $\rho\bar{E}$ . From these statistics a "95% safety factor" can be calculated as a multiplication factor that forces 95% of the model  $\hat{y}_i$  to equal or exceed the observed  $y_i$  for each model. This safety factor is computed as the reciprocal of the (antilog of the) 90% lower confidence limit for  $\bar{e}$ ; it provides one approach for scaling model predictions to achieve a defined level of safety in using these models in uncalibrated settings.

## RESULTS

### *Part I: Survey Evaluation*

The first part of the evaluation was based on working with the model developers to collect descriptive data on the models through the written, comparative model assessment described above. A table was prepared that included comparative data on six models: the three listed above plus the Conceptual Flowing Water and Reservoir Model developed by Dr. Henry Nelson of USEPA, a modified linkage of PRZM and EXAMS also developed by USEPA, and the USDA/NRCS AnnAGNPS. The tabular results of this exercise were summarized in an extensive table presented to the SAP team as background of the models and the evaluation (see <http://www.epa.gov/scipoly/sap/meetings/1998/july/matrix.htm>).

The evaluation process indicated that underlying algorithms for estimating pesticide fate and transport as well as hydrology appear to be very similar among the basin-scale models. Major differences in model capabilities exist with the incorporation of a linkage between ground and surface waters, foliar dissipation processes for pesticides, crop growth simulation, plant uptake of pesticides, and simulation of crop management practices. Other notable model capabilities are GIS interfaces with various databases (including loca-

tion of drinking water utilities) and model simulation capability of nonagricultural areas (e.g., forest and urban areas). The SAP made several comments and recommendations on the materials presented to them and on the proposed procedure for conducting the field evaluation. (For full comments, see FIFRA SAP meeting report July 1998: <http://www.epa.gov/scipoly/sap/1998/july/1part5.pdf>. The panel commented on (1) the models, (2) the evaluation plan, and (3) the White River model evaluation sites. Regarding the models, the SAP members stated their belief that the "complexity and sophistication do not necessarily equate to more accurate predictions in natural resource modeling, but that factors in this case, do call for the more sophisticated approach." They additionally stated that the EFED tiered modeling system calls for an increase in accuracy with each tier level, but it also calls for a different type of model. Specifically, the basin-scale methods call for consideration of a larger spatial scale (river basin), which involves processes not represented in the lower tier models. The panel also indicated that "integration of the models with site-specific GIS data, in many cases, would enhance the reliability and repeatability of the simulations."

In response to USEPA's question as to the whether the two subbasins of the White River watershed in Indiana could provide a reasonable evaluation, the panel stated that it believed that they would provide a reasonable first step in validation for that region due to the vast amount of data available as part of the NAWQA program plus the diversity of soils and LUs. They added that the data from the White River study can and should be used for model evaluation, but that two sets of data from a single geographic location are not sufficient to justify a complete validation because the natural, unexplained variability in water quality measurements is enormous. Thus, the basin-scale models selected for use in the basin-scale tier should be chosen with an emphasis on the amount and breadth of validation that has been conducted on the model. The major effort of developing water quality assessment technology is not the creation of the model, but rather the validation and testing that occurs at the back end of the project. Further, the panel stated that particular aspects of the White River data should be recognized during model validation. First, the measured pesticide concentrations were, according to the USGS report, among the highest in the nation. Secondly, the data showed an unusual relationship between soil type (i.e., drainage characteristics) and pesticide runoff. The more permeable watersheds, with a greater percentage of sandy soils, exhibited greater pesticide runoff than the less permeable watersheds. The panel also commented on the individual models. It pointed

out that, in general, it is important to recognize the limitations of the model simulation approach. Even with extensive efforts, the models will provide uncertain results. Overreliance on models should therefore be guarded against. The panel also commented on use of regression models stating that regression models in natural resources modeling applications generally underpredict the upper range (i.e., higher values) of the measured data; they do not predict the peaks. Specialized regression methods should be utilized to avoid this problem. They further cautioned that the past 30-year weather record is, from a historical perspective, a particularly calm period relative to variability and extreme events of rainfall. There is some evidence that our weather is again becoming more variable. The use of statistically based weather generators would help extend and amend the weather record.

## Part II: Model Field Evaluation

The second part of the evaluation was focused on the computer simulation of Sugar Creek in the White River watershed and matching model predictions to concentration values measured near the mouth of the creek. As the project team was based in many cities and communication was necessary to achieve a parallel evaluation procedure, regular phone conferences were held to coordinate each of the steps of the evaluation. Scheduling of phone conferences, distribution of conference minutes, and transfer of data were accomplished via the internet through a website setup for the project by the USGS. Conferences were held between each step of the evaluation to compare results and make decisions on methods to address unforeseen circumstances. *A summary of modeling experiences and a summary of the results of each model can be found in the JAWRA online ancillary data files (see Supplementary Material).*

## Comparative Results Among Models

Summary and performance statistics for observed and calibrated model flow, suspended sediment, and pesticide concentrations are presented in Table 5 through Table 9. In these Tables, italicized Pearson correlation coefficients are significant at the 1% level.

Statistics and model comparisons for 1993-1995 flow in Sugar Creek are given in Table 5. Both the mean (2.86 m<sup>3</sup>/s) and median (1.16 m<sup>3</sup>/s) observed flows are generally modeled within about 20% (with the exception of NPSM median flow, which is 152%) of observed. Correlation coefficients are positive and

significant at the 1% level, and the NS modeling efficiency coefficients are strongly positive for all three models. These outcomes are presumably necessary (although not sufficient) for successful modeling of the behavior of water-soluble pesticides (here

TABLE 5. Means and Standard Deviations of Observed and Simulated Flow During 1993-1995 in Sugar Creek With Comparative Statistics ( $n = 1,095$ ).

Statistic	Observed	NPSM	RIVWQ	SWAT
Mean (m <sup>3</sup> /s)	2.86	2.37	2.74	2.73
Standard Deviation (m <sup>3</sup> /s)	5.59	3.02	5.25	5.40
Median (m <sup>3</sup> /s)	1.16	1.77	0.92	1.07
Mean Absolute Error (m <sup>3</sup> /s)		1.72	1.60	1.34
Root Mean Square Error (m <sup>3</sup> /s)		3.75	3.13	2.87
Pearson Correlation Coefficient		0.79	0.84	0.86
Nash-Sutcliffe coefficient		0.55	0.69	0.74

Note: NPSM, Nonpoint Source Model; RIVWQ, Riverine Water Quality Model; SWAT, Soil Water Assessment Tool.

TABLE 6. Means and Standard Deviations of Observed and Simulated Suspended Sediment During 1993-1995 in Sugar Creek With Comparative Statistics ( $n = 61$ ) (data for RIVWQ Not Available).

Statistic	Observed	NPSM	SWAT
Mean (mg/l)	58.5	4.2	221.8
Standard Deviation (mg/l)	50.8	3.3	231.2
Median (mg/l)	43.0	3.5	127.0
Mean Absolute Error (mg/l)		54.3	170.9
Root Mean Square Error (mg/l)		73.4	269.1
Pearson Correlation Coefficient		0.38	0.40
Nash-Sutcliffe Coefficient		-1.1	-27.5

Note: NPSM, Nonpoint Source Model; SWAT, Soil Water Assessment Tool.

TABLE 7. Means and Standard Deviations of Observed and Simulated Atrazine During 1993-1995 in Sugar Creek With Comparative Statistics ( $n = 65$ ).

Statistic	Observed	NPSM	RIVWQ	SWAT
Mean ( $\mu$ g/l)	1.53	1.51	1.21	4.33
Standard Deviation ( $\mu$ g/l)	3.87	2.16	5.23	9.58
Median ( $\mu$ g/l)	0.20	0.58	0.03	0.31
Mean Absolute Error ( $\mu$ g/l)		1.98	1.75	3.30
Root Mean Square Error ( $\mu$ g/l)		4.17	5.47	8.14
Pearson Correlation Coefficient		0.12	0.30	0.64
Nash-Sutcliffe Coefficient		-0.18	-1.03	-3.50
Mean Log Proportional Error $e$		0.05	-1.63	-0.24
Standard Deviation $Se$		0.94	1.94	1.11
Geometric Mean Error $\bar{E}$		1.11	0.02	0.57
Standard Multiplier ( $\rho = 10^{Se}$ )		8.69	87.3	12.9
Percent Within 2X		28	14	22
95% Safety Factor		1.41	108.1	2.96

Note: NPSM, Nonpoint Source Model; RIVWQ, Riverine Water Quality Model; SWAT, Soil Water Assessment Tool.

TABLE 8. Means and Standard Deviations of Observed and Simulated Metolachlor During 1993-1995 in Sugar Creek With Comparative Statistics ( $n = 64$ ).

Statistic	Observed	NPSM	RIVWQ	SWAT
Mean ( $\mu\text{g/l}$ )	0.46	0.60	0.64	2.93
Standard Deviation ( $\mu\text{g/l}$ )	1.07	1.14	2.56	6.32
Median ( $\mu\text{g/l}$ )	0.10	0.19	0.01	0.26
Mean Absolute Error ( $\mu\text{g/l}$ )		0.70	0.62	2.51
Root Mean Square Error ( $\mu\text{g/l}$ )		1.45	2.27	6.24
Pearson Correlation Coefficient		0.14	0.46	0.57
Nash-Sutcliffe Coefficient		-0.84	-3.53	-33.4
Mean Log Proportional Error $e$		0.03	-1.77	0.22
Standard Deviation $Se$		1.06	2.30	0.99
Geometric Mean Error $\bar{E}$		1.08	0.02	1.66
Standard Multiplier ( $\rho = 10^{Se}$ )		11.37	201.5	9.72
Percent Within 2X		16	11	18
95% Safety Factor		1.53	178.6	0.97

Note: NPSM, Nonpoint Source Model; RIVWQ, Riverine Water Quality Model; SWAT, Soil Water Assessment Tool.

TABLE 9. Means and Standard Deviations of Observed and Simulated Trifluralin During 1993-1995 in Sugar Creek With Comparative Statistics ( $n = 20$ ).

Statistic	Observed	NPSM	RIVWQ	SWAT
Mean (ng/l)	7.20	15.19	7.01	7.38
Standard Deviation (ng/l)	3.30	15.72	14.78	6.39
Median (ng/l)	6.50	9.73	0.70	6.35
Mean Absolute Error (ng/l)		11.74	9.12	5.84
Root Mean Square Error (ng/l)		18.01	13.61	6.61
Pearson Correlation Coefficient		-0.16	0.35	0.14
Nash-Sutcliffe Coefficient		-30.2	-16.9	-3.2
Mean Log Proportional Error $e$		0.16	-0.93	-0.30
Standard Deviation $Se$		0.53	1.03	0.75
Geometric Mean Error $\bar{E}$		1.43	0.12	0.50
Standard Multiplier ( $\rho = 10^{Se}$ )		3.37	10.63	5.66
Percent Within 2X		30	10	35
95% Safety Factor		1.12	21.3	3.95

Note: NPSM, Nonpoint Source Model; RIVWQ, Riverine Water Quality Model; SWAT, Soil Water Assessment Tool.

atrazine and metolachlor) in the watershed. Model results for suspended sediment (necessary for accurate representation of more strongly sorbed pesticides, here represented by trifluralin) are less encouraging (see Table 6). Mean and median values for NPSM are an order of magnitude less than the observed data, and SWAT estimates are more than three times larger than observed. Although the models show significant correlation with observed sediment loads, the NS coefficients are negative, indicating the mean concentration (58.5 mg/l) is usually a better predictor of sediment load on each measurement date than is the corresponding model prediction.

Results for atrazine during 1993-1995 are given in Table 7. The observed and modeled means, medians, and standard deviations are not radically different

(with the exception of the RIVWQ median value of 0.03  $\mu\text{g/l}$ , almost an order of magnitude less than the observed value of 0.20  $\mu\text{g/l}$ ). Despite the positive correlations of the model estimates with observed atrazine concentrations (although that of NPSM is not statistically significant (significant at 17% level)), the NS coefficients are all negative, indicating the models do not succeed as well as the observed mean value as a descriptor of atrazine exposure concentrations. The MAE of the models all exceed the observed mean concentration of 1.53  $\mu\text{g/l}$ . The geometric mean proportional errors  $\bar{E}$  range from 0.02 (i.e., a model/observed ratio of 0.02, or estimates that are 2% of the observed values) for RIVWQ, to 1.11 for NPSM. Less than 30% of the predicted values fall within a  $\pm 2\times$  evaluation criterion. The model results could be scaled to ensure that 95% of model EEC are greater than or equal to the observed data by multiplication of NPSM, RIVWQ, and SWAT estimates by factors of 1.41, 108.1, and 2.96, respectively.

Similar results are seen for metolachlor, the other water-soluble pesticide studied (Table 8). Mean EEC differ more for metolachlor than was seen in the results achieved for atrazine, however (compare Table 7). Both the NPSM mean and its median EEC exceed the observed values by a relatively small margin (NPSM mean EEC of 0.60  $\mu\text{g/l}$  vs. 0.46  $\mu\text{g/l}$  observed; median EEC of 0.19  $\mu\text{g/l}$  vs. 0.10 observed). Although the mean EEC for RIVWQ (0.64  $\mu\text{g/l}$ ) is also near the observed value of 0.46  $\mu\text{g/l}$ , the median RIVWQ EEC of 0.01  $\mu\text{g/l}$  is a full order of magnitude less than the observed value (0.10  $\mu\text{g/l}$ ). As was in the case for atrazine, the predicted values are positively correlated with the observed (although that for NPSM is only statistically significant at the 13% level), but the NS coefficients are all negative. The geometric mean error for RIVWQ is the same as that found for atrazine (0.02), but both NPSM and SWAT estimates on average exceed the observed data (i.e., their geometric mean errors  $\bar{E}$  are  $> 1.0$ ). Although  $< 20\%$  of the estimates for any of the models are within  $2\times$  of the observed, 95% of SWAT EEC equal or exceed observed values without application of a safety factor (i.e., the multiplicative safety factor in Table 8 is  $< 1.0$ ). For NPSM, the same objective could be achieved by multiplication of NPSM EEC by 1.53, and, for RIVWQ, by multiplication of RIVWQ EEC by a factor of approximately 180.

Mean RIVWQ and SWAT EEC for trifluralin (Table 9) differ from observed values by only  $\sim 5\%$ ; the NPSM mean EEC is more than twice the observed value. The median EEC for RIVWQ (0.70 ng/l) is, however, again in an order of magnitude less than that observed (6.50 ng/l). None of the correlation coefficients are statistically significant (note, however, that only 20 observations were

available for study, as against >60 for atrazine, metolachlor, and suspended sediment. The correlation coefficient for NPSM is negative [ $r = -0.16$  (not, however, statistically significant)]. The NS coefficient is again strongly negative for all three models. The geometric mean errors indicate that NPSM generally overestimates trifluralin exposure ( $\bar{E} = 1.43$ ), while RIVWQ and SWAT underestimate ( $\bar{E} = 0.12$  and  $0.50$ , respectively). Performance of the models in terms of the fraction of EEC within a factor of two is best for this pesticide, reaching 35% for SWAT. Safety factors, which account for both the mean and the variance of the errors, range from 1.12 for NPSM through 3.95 for SWAT to 21.3 for RIVWQ.

## CONCLUSIONS

The USEPA OPP has historically used a static water body for aquatic ecological pesticide exposure assessment and a steadily flowing reservoir for public drinking water exposure assessment in evaluating possible pesticide risk from surface water. This basin scale, flowing water model evaluation process was a valuable first step for the USEPA in planning for assessments using flowing water models and scenarios. It was also a valuable experience for the model developers in assessing strengths and weaknesses of the models with the goal of improving modeling processes where possible. The evaluation provided insights into the difficulties of attempting to match weekly monitoring results with daily time step models. The following conclusions are related to a variety of topics and are numbered not in relative order of importance but in order to provide additional focus on each of them.

(1) This exercise was performed as a model evaluation and as a model validation. The comments of the FIFRA SAP are very relevant to the interpretation of this exercise. The SAP stated that "two sets of data from a single geographic location are not sufficient to justify a complete validation because the natural, unexplained variability in water quality measurements is enormous." "Thus, the basin-scale models selected for use in the basin-scale tier should be chosen with an emphasis on the amount and breadth of validation that has been conducted on the model." The USEPA is therefore not considering that this work represents either a validation or an invalidation of these models.

(2) Simulation of pesticide environmental fate and transport in flowing water in an agricultural watershed is a substantially more complex endeavor than current simulation in a static water body. This com-

plexity is due to the larger size of the watersheds simulated, the number of soils present and variability of soil properties, the spatial and temporal variability of application across the watershed, the variability of vegetative cover, the variability of slopes and irregularities of the land surface, the inability of a few weather stations to adequately represent the spatial variability and the dynamic, mobile character of rainfall events, and channel processes that are variable in space and dynamic in time.

(3) Basin-scale simulation is a very data-intensive, time-consuming and therefore expensive process, which may militate against its wide-scale usage in the near future.

(4) Sediment-bound pesticides are the most difficult to simulate due to reduced availability of sediment data, which is needed for calibration and the rapid variability of suspended sediment as flow changes. Simulation of trifluralin was less accurate than that of atrazine and metolachlor with all three models.

(5) While there were differences between the capabilities of the models to simulate certain processes, there were also differences in the accuracy with which certain rainfall/runoff events could be simulated. Certain storm events were substantially less accurately predicted with all three models. The reasons for this have not been explored but are likely to center on events for which conditions in the field are most inadequately represented by the simplifying assumptions of the models. The actual spatial and temporal variability of rainfall across a watershed, for example, may have profound effects in the field that very poorly represented by the models.

(6) All three models predicted runoff events and pesticide peaks based on certain recorded rainfall events that were not recorded in the field monitoring because they occurred between weekly samples. In this instance, the models were an aid to identifying the timing of runoff events that were not identified in the less frequent monitored values.

(7) Capability to simulate tile drainage is an essential component of a basin-scale model. NAWQA data recorded in the White River basin show that pesticide concentrations were two times higher in portions of the basin with permeable soils. Furthermore, the tile drains were found to play a major role in the transport of pesticides in poorly drained soils, especially during wet growing seasons. These points reinforce earlier concerns that the basin models must have a tile-drain component. Without such a component, the contributions of poorly drained soils to pesticide concentrations in streams are likely to be underestimated.

(8) Local pesticide usage data can be disaggregated to provide estimates of daily application amounts

across a large area. For pesticides that are applied at or near planting dates (e.g., pre-plant, in-furrow), such estimates can be made using the percent of total acres planted. In other cases, professional judgment (expert opinion) may be the only basis for disaggregating usage over a time window. Correct application timing estimates may be especially important when intensive planting is closely followed by a major storm event.

(9) The needs of modeling should be considered during the planning phase of monitoring programs. This would allow collection and recording of ancillary data needed for modeling and might impact the sampling schedule.

(10) Rigorous statistical techniques that are independent of model-developer or model-user bias and of the magnitude of the values predicted can make a substantial contribution in assessing both the accuracy and precision of model estimates (Burns, 2001). This provides a very useful enhancement to the visual inspection of time series graphical results.

## NEXT STEPS

(1) As pointed out by the SAP, an evaluation focused on one or two sites is insufficient to make major decisions about a model or models. Repetition of a similar model evaluation using a wider variety of sites would be a useful exercise.

(2) Adequate temporal and spatial data to represent soils, topography, man-made features (tile drains, altered channel geometry, and small dams), application amount and timing and rainfall amount and timing are crucial to simulating pesticide runoff. New evaluation exercises should be planned that specifically address these data issues.

(3) An exercise similar to this one could be repeated in conjunction with development of the "next-generation" of pesticide transport and fate modeling tools. Lessons learned from this work would provide a good basis for new models or new features in existing models. Use of spatial representations of rainfall data now available from radar imagery would reduce one of the difficulties of addressing this type of spatial variability.

(4) This exercise was based on using modeling primarily to determine the magnitude and frequency of occurrence of pesticide concentrations, rather than to explore alternative management scenarios. The deterministic models used in this analysis are very detailed in the processes they incorporate, but this virtue would also be of value in cases where evaluation of alternative management scenarios is required.

(5) Given the stated objective of determining exposure, it is possible that statistical models based on sampled data, which have recently become available, could be useful for predicting magnitude and frequency of occurrence. Statistical (i.e., empirical) models can be applied at much larger scales, allowing for greater diversity in watershed characteristics. They produce direct measures of error, and they are somewhat immune (in terms of bias) to errors in the input data (which, in the case of pesticide application based on state data, are likely to be quite large at the relatively small scale the models are applied).

## ACKNOWLEDGMENTS

The authors of this paper wish to acknowledge the USEPA Office of Pesticide Programs for funding this comparative modeling assessment and the publication of this paper. The authors further wish to thank the USDA-Agricultural Research Service, Temple, Texas; USEPA Office of Research and Development, Athens, Georgia; National Oceanographic and Atmospheric Administration, Lajas, Puerto Rico; Texas A&M University, College Station, Texas; and Waterborne Environmental, Inc., Leesburg, Virginia, for providing the time and resources required for completion of this work and the publication of this report. We would like also to acknowledge the immense contribution of Charles G. Crawford, Surface Water Status and Trends Coordinator, National Water Quality Assessment Program, USGS Indianapolis, Indiana for providing monitoring data and for his overall support and comments throughout the evaluation process.

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## SUPPLEMENTARY MATERIAL

Supplementary materials mentioned in the text are available as part of the online paper from: <http://www.blackwell-synergy.com>.

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